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# Wave damping by monomolecular surface films and their chemical structure. Part I: Variation of the hydrophobic part of carboxylic acid esters

by Heinrich Hühnerfuss,<sup>1</sup> Philipp Lange<sup>2</sup> and Wolfgang Walter<sup>1</sup>

## ABSTRACT

Plunger generated 1.0, 1.3, 1.8, 2.0, 2.3, and 2.5 Hz waves have been used to investigate the direct wave damping effect of carboxylic acid ester surface films. The correlation between the damping coefficient  $\Delta$  and frequency  $f$  obeys an exponential law  $\Delta = \Delta_0 \cdot e^{-Bf}$ . Systematic variation of the ester alcohol component shows that surface films of lower alkyl chain derivatives (palmitic acid methyl ester [PME], -ethyl ester [PEE]) contribute to wave energy dissipation by an E-/Z-isomerization mechanism during wave induced dilatation and compression of the film, whereas esters with longer alcohol alkyl chain are preferably oriented in the E-form. By introducing a branched alcohol component instead of a straight chain one wave damping is decreased. Stepwise prolongation of the carboxyl acid alkyl chain between C<sub>14</sub> and C<sub>22</sub> shows a maximum in wave damping to occur at C<sub>18</sub> (palmitic acid methyl ester [PME]). Introduction of one to three C=C-groups (oleic acid methyl ester [OLME]; linolenic acid methyl ester [L3ME]) induces a significant decrease of the wave attenuation effect compared to the saturated compound (stearic acid methyl ester [SME]), but no difference is discernible between OLME and L3ME. C=C-E-oriented derivatives (elaidic acid methyl ester [ELME]) and C=C-Z-oriented ones (oleic acid methyl esters [OLME]) also show the same wave damping characteristics.

## 1. Introduction

The widespread occurrence of natural surface films has been pointed out by several authors. The analytical evaluation of the carboxylic acid composition (Brockmann *et al.*, 1976; Garrett, 1967; Kattner and Brockmann, 1978; Marty *et al.*, 1979; Williams, 1961) or the surface tension lowering effect of these compounds measured by Adam's (1937) spreading oil method (Barger *et al.*, 1974; Hühnerfuss *et al.*, 1977; Lumby and Folkard, 1956) has been used as an indicator for the presence of natural surface active material. Apart from the carboxylic acid

1. Institut für Organische Chemie und Biochemie der Universität Hamburg, Martin-Luther-King-Platz 6, 2000 Hamburg 13, Federal Republic of Germany.

2. Bundesanstalt für Wasserbau, Wedeler Landstr. 157, 2000 Hamburg 56, Federal Republic of Germany.



composition little is known about other chemical compounds of natural surface films. It is generally accepted that these surface active compounds are produced by the secretions of zoo- and phytoplankton, and in addition a smaller portion may be secreted by higher plants or animals of the ecological chain (Deacon, 1979).

The primary influence of these films is their wave damping ability which in turn modifies several additional air sea interaction processes (Hühnerfuss and Lange, 1975). These effects allowed several authors to use well defined artificial surface films as an oceanographic tool for studying mechanisms of different processes (for reviews see Hühnerfuss and Garrett (1981)). In recent research the modification of backscattered radar signals by monomolecular surface films has received increased attention (Hühnerfuss *et al.*, 1978; Hühnerfuss *et al.*, 1981).

The mechanism of the wave damping effect is not fully understood since three different terms have to be considered: a direct influence of surface films (viscous damping), and two secondary terms, i.e., the modification of the interaction between wind field and wave field and of long wave/short wave coupling (Hühnerfuss *et al.*, 1981).

In this work we concentrate on the direct influence of surface films giving a first systematic survey of the correlation between the chemical structure of the hydrophobic part of surface films and its influence on wave damping. On account of the widespread occurrence of carboxylic acid derivatives in natural surface films the hydrophilic part of the surface active substances will be an ester group.

## 2. Theory of wave damping by surface films

Phillips (1977) described a wave damping theory which was supposed to be generally valid because no dependence on the chemical structure of the film forming substances had to be assumed, but experimental data are not consistent with this theory (Hühnerfuss *et al.*, 1981). Other authors considered energy dissipation occurring only by viscosity effects within the film itself (Bendure and Hansen, 1967; Dorrestein, 1951; Goodrich, 1961, 1962; Lucassen and Hansen, 1966; van den Tempel and van de Riet, 1965). Another group of investigators tried to take into account the physical processes occurring between the bulk water and a monolayer during passage of a wave (Drost-Hansen, 1972; Garrett and Zisman, 1970; Horne, 1972; Vollhardt and Wüstneck, 1978). These latter trials are supposed to bear the more encouraging perspectives. A working group of the "Symposium on capillary waves and gas exchange" in Trier (FRG) 1979 (Broecker and Hasse, 1980) concluded that the complete expression for the Gibbs enthalpy, including the energy and entropy effects resulting from reorientation of the film molecules and from changes in film concentration, should be evaluated and its time dependence be treated with the methods of irreversible thermodynamics.

In this paper we confine ourselves to the correlation between the chemical

structure and the widely accepted damping coefficient  $\Delta$ , where  $\Delta$  is the exponent of the exponential function describing the damping to a wave with an amplitude  $a_0$  at a fetch zero and  $a_x$  after a distance  $x$ :

$$a_x = a_0 e^{-\Delta x} . \quad (1)$$

In order to gain insight into the contribution of the three terms of wave damping (direct effect, modification of wind field/wave field, modification of long/short wave coupling) to waves of different wave lengths, the frequency dependence of  $\Delta$  is also investigated in this work. The correlation between the frequency  $f$  and the damping coefficient for a clean surface  $\Delta_c$  and for short waves ( $L < 0.5$  cm) can be derived from hydrodynamic theory (Davies and Rideal, 1963):

$$\Delta_c = 8\pi\eta f/3\gamma , \quad (2)$$

where  $\eta$  is the viscosity and  $\gamma$  the surface tension of water. This expression indicates that  $\Delta_c$  should linearly increase with frequency. In the presence of a surface film, however, this equation cannot be valid, since in addition to viscous damping other terms contribute to wave damping as well. In order to take into account some of the more important additional terms contributing to wave damping in the presence of a surface film, Cini *et al.* (1982) introduced a damping ratio function  $y(f)$  as a correlation factor, which contains the surface dilatation modulus

$$E e^{j\psi} = - \frac{d\gamma}{d \ln A} , \quad (3)$$

where  $A$  is area/molecule. Parameters  $E$  and  $\psi$  are assumed to be slowly varying functions of frequency, the evaluation of which depends on the solubility of the surface film. An explicit derivation for both soluble and insoluble surface films is given by Cini *et al.* (1982). In this paper, only the basic assumptions can be repeated: in the case of a soluble surface film, the thermodynamic equilibrium is assumed to exist within the subsurface, the process being essentially diffusional. So equation (3) can be modified to

$$E e^{j\psi} = E_0 \left( \frac{\ln \Gamma}{\ln A} \right) , \quad (4)$$

where  $\Gamma$  the surface film concentration,  $E_0$  the elasticity modulus. The second term on the right hand side of (4) accounts for adsorption or desorption variations during surface compression and dilatation due to wave action.

For insoluble surface films in lieu of the diffusional process a similar process has been assumed, which Cini *et al.* (1982) call "directional packaging." The concept involves the packaging density distribution,  $c_P$ , to be a function of the vertical coordinate, and a structural parameter,  $D_P$ , having dimension of a diffusional coefficient (for details see Cini *et al.*, 1982).



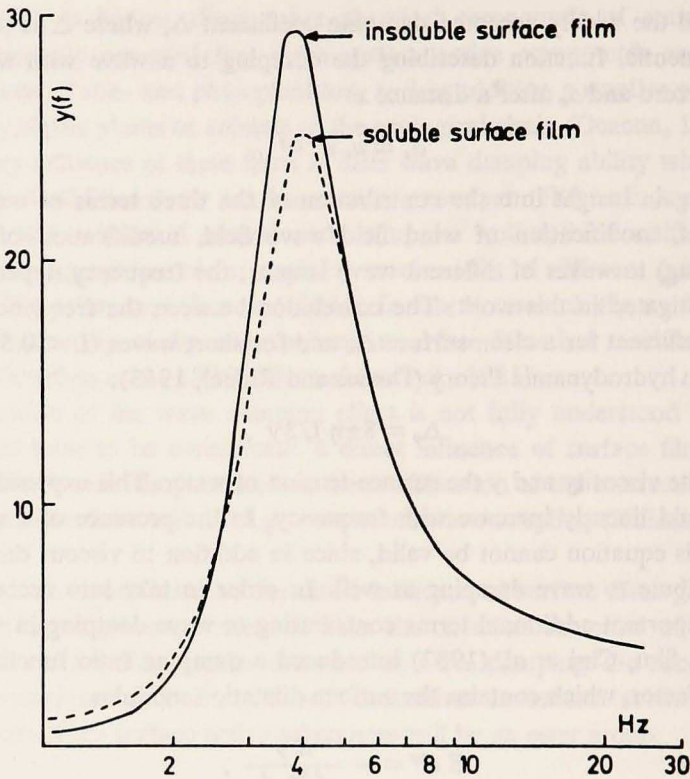


Figure 1. Calculated damping ratio  $y(f)$  vs. frequency for an insoluble (—) and a soluble (----) surface active substance, assuming in both cases an elasticity modulus  $E_o = 36.5$ .

A calculation of the damping ratio function  $y(f)$  based on these assumptions showed for both soluble and insoluble surface films that for all cases  $y(f)$  passes through a maximum  $y_M$ . This is exemplarily shown in Figure 1 for a soluble and an insoluble surface active compound with  $E_o = 36.5$ .

The above summarized derivations allow a conceivable explanation of some phenomena observed in the presence of surface films. A complete description of the influence of surface films on the air-sea boundary, however, has to include the modification of the upper water layer. A promising approach has been proposed by Alpers *et al.* (1982), who calculated the alteration of the dielectric properties in the presence of a surface film: it turned out that the "surface" dielectric constant may increase by orders of magnitude, which is attributed to a surface film induced polarization of the water molecules adjacent to the surface active compound. In addition, a surface film creates a new anomalous dispersion regime (dielectric

relaxation) which lies below the relaxation frequency of free water  $f_0$ . These re-orientation effects of water molecules due to wave action in the presence of a monolayer are expected to contribute considerably to wave energy dissipation. Additional investigations are, however, necessary in order to combine the theoretical approaches of wave damping both of Cini *et al.* (1982) and of Alpers *et al.* (1982).

### 3. Experimental procedure

Prior to each experiment which was performed in our wind wave tank (Hühnerfuss *et al.*, 1976) the water surface was thoroughly cleaned by blowing all potentially disturbing surface active pollutants to the downwind end of the tank where they could be sucked off by a perforated tube connected to a vacuum pump. The thoroughness of the cleaning procedure could be controlled visually by the appearance of high frequency capillary waves and by surface tension measurements after Adam (1937).

Tap water was used for the experiments instead of sea water. Natural sea water could contain organic material which would substantially disturb the experiment. In our case, the results obtained in the presence of tap water and *pure* sea water are assumed to be comparable, since salinity is known to modify surface tension only slightly (for details see Hühnerfuss *et al.*, 1977) and the alkalinity of sea water (pH ca. 8.0-8.3) would not lead to significant hydrolysis of the surface film forming substances within the short periods of the single experiments (about 6 min.). The difference in viscosity of about 7% between tap water and sea water can be neglected in our studies, since we used relatively short-lived gravity waves.

The wave damping effect of each substance was investigated such that plunger-generated waves of 1.0, 1.3, 1.8, 2.0, 2.3, and 2.5 Hz were allowed first to propagate over a carefully cleaned water surface and then over a surface covered with a surface film. The amplitudes of the waves were measured by resistance wave gauges of the Danish Hydraulic Institute, Horsholm (Denmark), at distances of 3.5 m, 7.5 m, 11.5 m, and 15.5 m from the point where the film was dropped onto the water surface. Care had to be taken to produce only small amplitude waves so that the frequency of the waves did not change with travel distance. This was controlled by online FFT analysis of the wave staff outputs. For high amplitudes a broadening of the initially sharp spectral peak would occur at the longer distances attributed to non-linear interactions, which would bias our data. A 15 minute pause was made between each measurement to allow for the damping out of circulating water movements within the tank. The wind generator was turned off in this experiment.

Surface films of carboxylic acid esters (Table 1) were spread from a spreading solvent (75 mmol of distilled n-heptane or ethanol, depending on solubility) by continuously pumping the solution onto the water surface by an exactly dosing tube



Table 1. Direct influence of carboxylic acid ester surface films on 1.0, 1.3, 1.8, 2.0, 2.3, and 2.5 Hz water waves. (+) indicates significant wave damping was measured, (-) no significant damping was measured.

substance (abbrev.)	frequency (Hz)					
	1.0	1.3	1.8	2.0	2.3	2.5
Tetradecanoic acid methyl ester (TDME)	-	-	-	-	+	+
Palmitic acid methyl ester (PME)	-	-	+	+	+	+
Palmitic acid ethyl ester (PEE)	-	-	+	+	+	+
Palmitic acid propyl ester (PPE)	-	-	+	+	+	+
Palmitic acid isopropyl ester (PIPE)	-	-	-	-	-	+
Palmitic acid butyl ester (PBUE)	-	-	-	-	-	-
Palmitic acid hexadecyl ester (PCEE)	-	-	-	-	-	+
Stearic acid methyl ester (SME)	-	-	+	+	+	+
Oleic acid methyl ester (OLME)	-	-	-	-	-	-
Elaidic acid methyl ester (ELME)	-	-	-	-	-	-
Linolenic acid methyl ester (L3ME)	-	-	-	-	-	-
Eicosanoic acid methyl ester (EIME)	-	-	-	-	-	+
Docosanoic acid methyl ester (BHME)	-	-	-	-	-	-

pump such that an excess of the surface active material was available for repairing any hole that might occur. Continuous pumping was necessary because surface films of substances with lower spreading velocities would slowly move toward the beach by wave induced Stokes drift.

The carboxylic acid esters (Table 1) were prepared by the method of Einhorn (Autorenkollektiv, 1964) by reaction of the carboxylic acid chlorides and the alcohols in pyridine. The need for exceptional purity in these studies necessitated the redistillation or recrystallization of the substances until a gaschromatographically controlled purity of at least 99% was achieved. Elaidic acid methyl ester (ELME) was supplied by FLUKA, Neu Ulm (FRG).

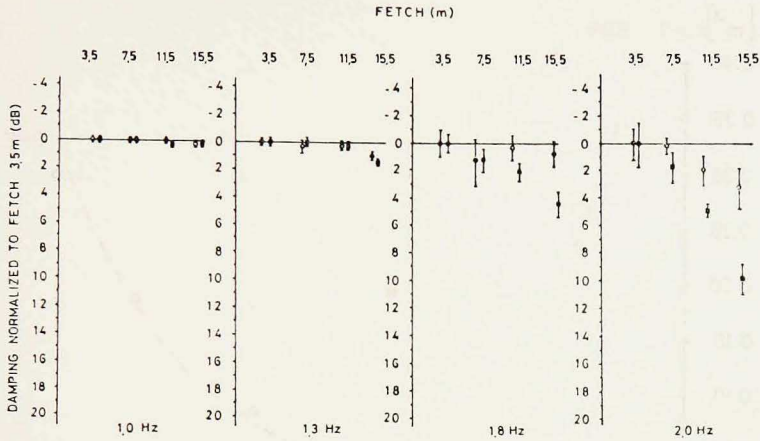


Figure 2. Wave amplitudes [dB] normalized to a fetch of 3.5 m vs. fetch [m]. Data of 1.0 Hz, 1.3 Hz, 1.8 Hz, and 2.0 Hz plunger generated waves of a clean water surface (○) and a surface covered with a palmitic acid propyl ester surface film (■) are given. The fetches represent the distances from the point where the films dropped onto the water surface.

#### 4. Results and discussion

*a. Frequency dependence of  $\Delta$ .* A sample of the wave amplitude data for a clean water surface and for a surface covered with a palmitic acid propyl ester surface film [PPE] are shown in Figure 2. On account of the intensive damping effect only the values of 1.0, 1.3, 1.8, and 2.0 Hz are given. The amplitudes (in dB) are averages (with standard deviation) over a measurement interval of 5.3 minutes and are normalized to the first measuring point at a fetch of 3.5 m. The main reason for the lower error bars in comparison to those given in an earlier publication (Hühnerfuss *et al.*, 1981) is supposed to be the pause between each measurement as mentioned above.

Figure 2 shows that PPE causes a significant damping at a wave frequency of 1.8 Hz and higher. In an analogous manner, the frequency range of a direct influence for various carboxylic acid esters has been measured. The results are summarized in Table 1.

In order to get quantitative information on the direct influence of carboxylic acid ester surface films on 1.0-2.5 Hz water waves, damping coefficients  $\Delta$  have been calculated and plotted vs. frequency. In Figure 3 the values for the relatively intensively damping substance PPE and a substance with no significant effect in the frequency range 1.0-2.5 Hz palmitic acid butyl ester [PBUE] are given as an example for all substances investigated in this work. The regression curves fairly well follow an exponential law

$$\Delta = \Delta_0 \cdot e^{-Bf}, \quad (5)$$



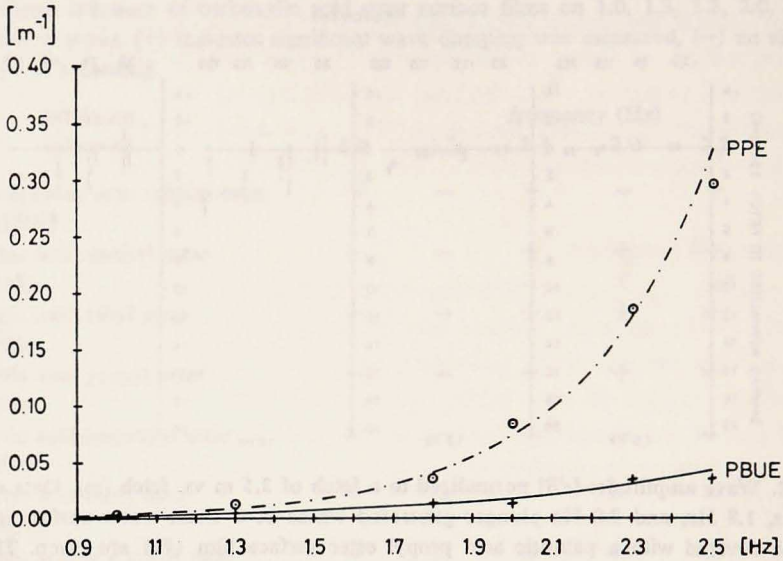


Figure 3. Frequency dependence of damping coefficient  $\Delta$  [ $\text{m}^{-1}$ ] of palmitic acid propyl ester ( $\odot$  - · · · · ·  $\odot$  PPE) and palmitic acid butyl ester ( $+$  —————  $+$  PBUE). Coefficients of determination: PPE = 0.986; PBUE = 0.970.

where  $\Delta_0$  and  $B$  are regression coefficients. The coefficients of determination are 0.986 (PPE) and 0.970 (PBUE). In the following figures we only plot the regression curves in order not to overload the figures with data points.

An exponential law for  $\Delta$  instead of the linear correlation observed on a pure water surface is qualitatively in agreement with the curves calculated for the corrective factor  $y(f)$  (see Fig. 1), which accounts for the presence of a monolayer in a wave field: with an elasticity modulus  $E_0 = 36.5$  the curve  $y(f)$  follows an exponential law until reaching the maximum at a frequency of about 4 Hz.

*b. Structural variation of the ester alcohol component.* The observed difference in the wave damping effect of PPE and PBUE (see Fig. 3) was the basis for a systematic investigation where the length of the alkyl chain of the ester alcohol component was stepwise prolonged. The results are summarized in Figure 4. Palmitic acid methyl ester [PME] and palmitic acid ethyl ester [PEE] nearly show the same wave damping effect in the frequency range 1.0-2.5 Hz, whereas the damping coefficients of PPE are significantly lower. The minimum damping effect of this homologous series is observed with PBUE. A further lengthening of the alcohol  $\text{CH}_2$ -chain leads to a slight increase of the wave damping effect as seen with the palmitic acid hexadecyl ester [PCEE] curve.

The explanation for the variation in the wave damping effect of the palmitic acid ester derivatives can be drawn from Langmuir-curves (Fig. 5): it is well established

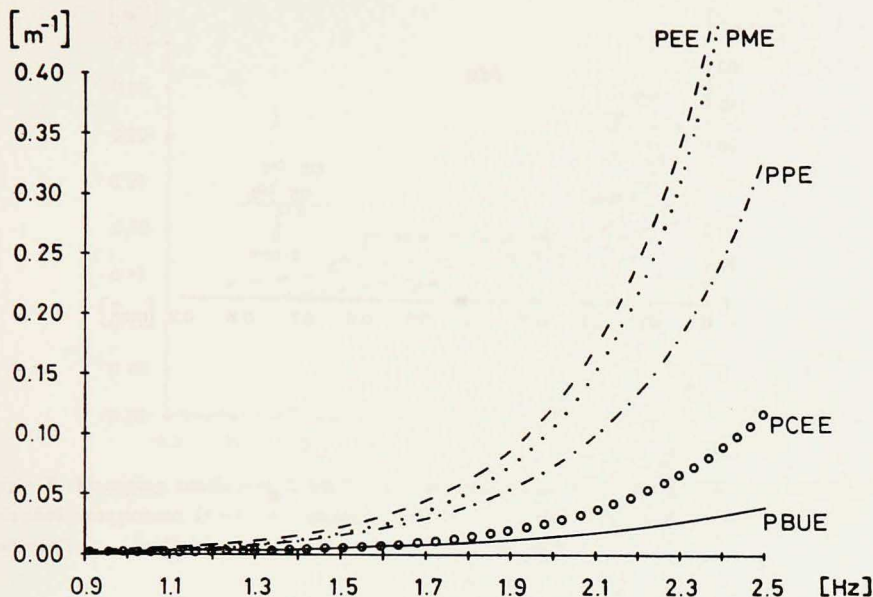


Figure 4. Damping coefficient  $\Delta$  [ $\text{m}^{-1}$ ] vs. frequency [Hz]. Comparison of palmitic acid ester derivatives with increasing alkyl chain length of the alcohol component (----- palmitic acid ethyl ester PEE / ..... palmitic acid methyl ester PME / ······ palmitic acid propyl ester PPE / oooo palmitic acid hexadecyl ester PCEE / ————— palmitic acid butyl ester PBUE).

(Alexander and Schulman, 1937; Alexander and Rideal, 1937) that a PEE monolayer can exist in two different isomers. At low concentrations, the *E*-form is stabilized, i.e., the normally energetically less preferred form (Hühnerfuss, 1971) in dilute solutions. When the PEE surface film is compressed, the ethyl chain is pushed into the water beneath the ester group thus sheltering the ester carbonyl from both  $\text{H}_2\text{O}$  solvation and  $\text{OH}^-$  attack (see Alexander and Rideal (1937)). This *E*-/*Z*-isomerization has been previously established by comparing the surface potentials and velocity constants of hydrolysis in both *E*- and *Z*-form (Alexander and Schulman, 1937). In the long range (see Fig. 5) between the pure *E*- and *Z*-forms an equilibrium between both forms can exist. The observed damping coefficients of PEE suggest that an alteration of the available area/molecule during passage of a wave is large enough so that a continuous *E*-/*Z*-isomerization can occur, i.e., at least the equilibrium range must be reached during dilatation (Fig. 5).

If the alcohol alkyl chain is prolonged (PBUE), the lateral adhesion between it and the acidic alkyl chain becomes more important thus further stabilizing the *E*-form until the *E*-/*Z*-isomerization no longer can contribute to wave damping. The slight increase of the wave attenuation effect in the presence of a PCEE surface



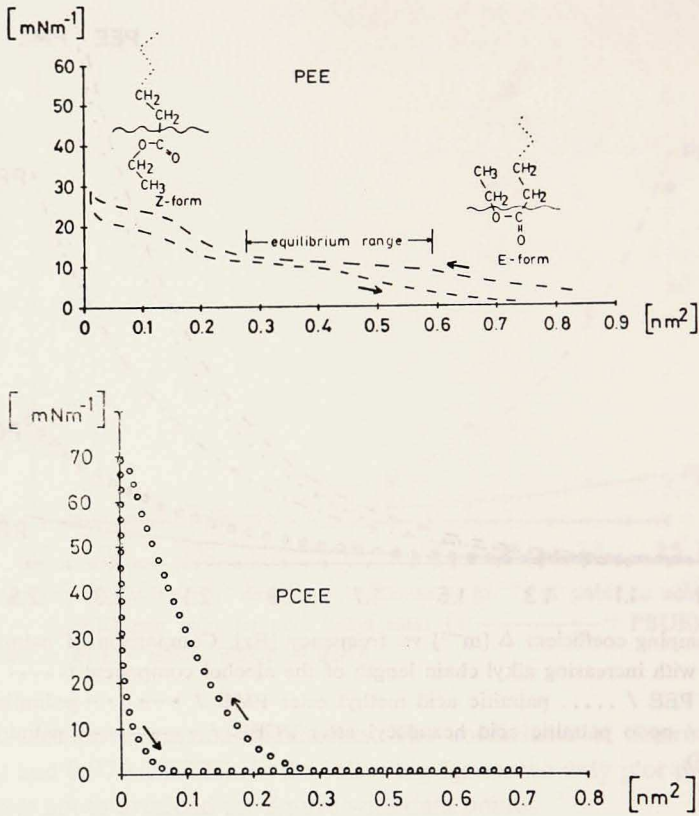


Figure 5. Langmuir-curves (surface pressure  $[\text{mNm}^{-1}]$  vs. available area/molecule  $[\text{nm}^2]$ ) of palmitic acid ethyl ester (---- PEE) and palmitic acid hexadecyl ester (ooooo PCEE). The steep PCEE-curve is typical for a condensed phase state, whereas PEE shows a liquid expanded state characteristic.

film is attributed to the phase change from the expanded to a condensed phase state. This phase change can be concluded from Langmuir-curves of PCEE (Fig. 5), which show the characteristic shape of a condensed phase surface film.

A hindrance for the E-/Z-isomerization also seems to exist, if a branched alcohol component is introduced instead of a straight chain alcohol component. A comparison between palmitic acid n-propyl ester [PPE] and palmitic acid isopropyl ester [PIPE] (Fig. 6) shows the significantly lower damping effect of PIPE. For the moment it is unclear whether the E- or Z-form of PIPE is preferred. This will be clarified by additional surface potential measurements.

*c. Structural variation of the carboxylic acid alkyl chain.* Apart from palmitic acid hexadecyl ester [PCEE] which has been found in coral mucus secretions (Benson

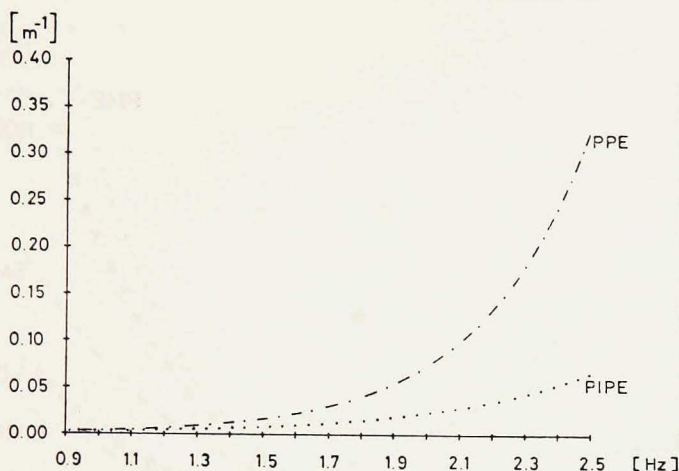


Figure 6. Damping coefficient  $\Delta$  [ $\text{m}^{-1}$ ] vs. frequency [Hz]. Comparison between straight chain alcohol component (•-•-•- palmitic acid propyl ester PPE) and branched alcohol component (..... palmitic acid isopropyl ester PIPE) of palmitic acid esters.

and Muscatine, 1974) not much is known about the alcohol component of the carboxylic acid esters of natural surface films. Very detailed information, however, is available about the fatty acid components of several natural surface films (Brockmann *et al.*, 1976; Garrett, 1967; Kattner and Brockmann, 1978; Marty *et al.*, 1979; Williams, 1961). Structural variations, which were found in fatty acids of natural films, based on variation of alkyl chain length and the presence of one to six C=C-bonds. The influence of these structural parameters on wave damping has also been investigated in this work.

The contribution of prolongation of the alkyl chain of the fatty acid component to wave damping is shown in Figure 7. The alcohol component is  $\text{CH}_3\text{-OH}$  for all substances. The maximum wave damping is achieved with a palmitic acid methyl ester surface film [PME], less wave damping is observed when a stearic acid methyl ester [SME] or tetradecanoic acid methyl ester [TDME] monolayer is present. A further prolongation of the alkyl chain up to  $\text{C}_{22}$ , docosanoic acid methyl ester [BHME], leads to a steady decrease of the wave attenuation effect. A conceivable explanation for the maximum of wave damping occurring at a  $\text{C}_{16}$  chain length may be the optimum elasticity of this compound: when prolonging the chain length, the cohesion between the alkyl chain increases such that the surface film may partially rupture due to wave action. Repairing of these "holes" is also inhibited due to increasing cohesion, i.e., the spreading velocity approaches zero. Consequently zones may occur which cannot contribute to wave damping. On the other hand, shortening of the alkyl chain (TDME) lowers the cohesion and the attractive forces between the alkyl chain to a degree that repairing of wave-induced



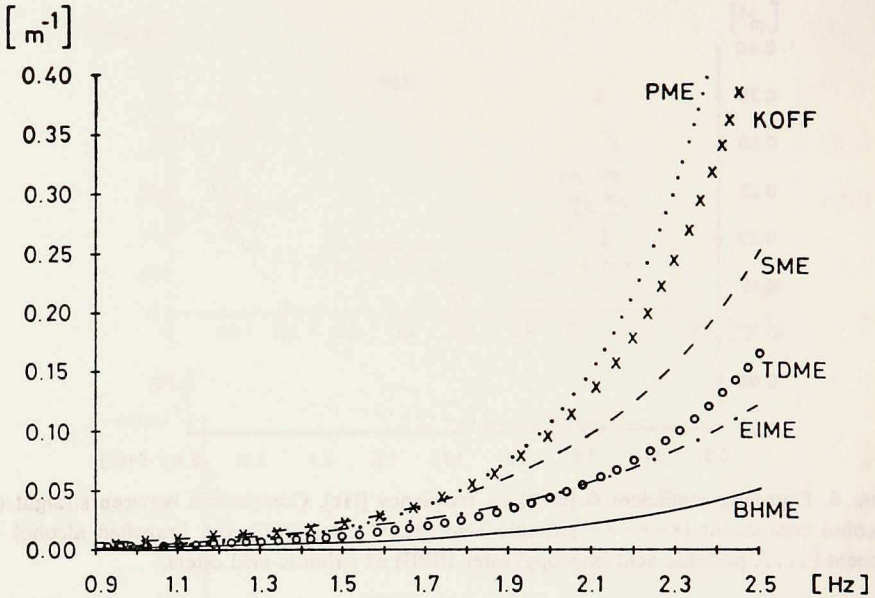


Figure 7. Damping coefficient  $\Delta$  [ $\text{m}^{-1}$ ] vs. frequency [Hz] of surface films consisting of different methyl esters of homologous carboxylic acids (..... palmitic acid methyl ester PME / ----- stearic acid methyl ester SME / ooooo tetradecanoic acid methyl ester TDME / -.-.-.- eicosanoic acid methyl ester EIME / ————— docosanoic acid methyl ester BHME / XXXX KOFF mixture).

holes is also inhibited. This effect is obviously not completely balanced by the better respreading abilities of the shorter chain compounds (e.g., extrapolated spreading velocity of TDME measured at 293 K :  $17.3 \text{ cm s}^{-1}$ ). The optimum between both cohesion and respreading ability seems to occur at a  $\text{C}_{16}$  chain length.

It is worth mentioning that the above cited authors who analyzed natural surface films found them to contain mostly palmitic acid and stearic acid derivatives, i.e., exactly those components with alkyl chain lengths contributing most to wave damping. This may support some speculations on the role of natural surface films in ecological systems, e.g., in reef ecology, where they may produce quieter water conditions beneficial to delicate coral forms or plankton species (Deacon, 1979).

The introduction of unsaturated  $\text{C}=\text{C}$ -groups leads to a significantly lower damping effect (Fig. 8), as has been shown by comparison of stearic acid methyl ester [SME] with oleic acid methyl ester [OLME]. Two additional  $\text{C}=\text{C}$ -groups (linolenic acid methyl ester [L3ME]) compared to OLME do not make any difference in the wave damping characteristics. A tentative explanation for the different wave damping ability of saturated and unsaturated surface active compounds is the significantly lower cohesion between unsaturated alkyl chains due to steric hindrances. This

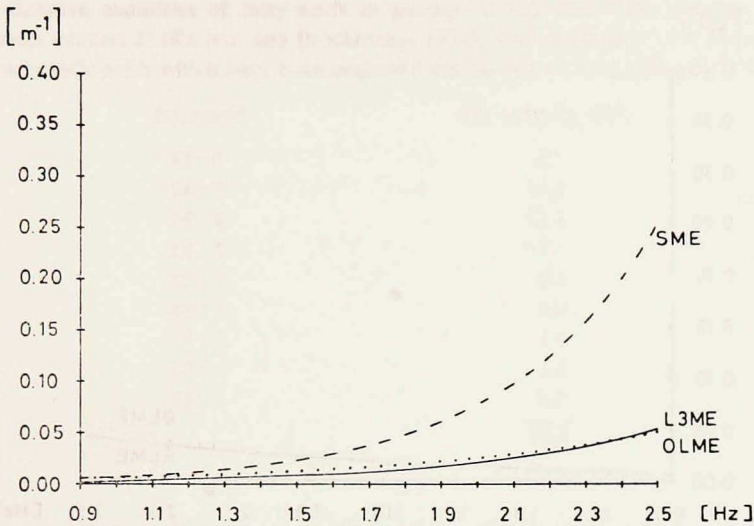


Figure 8. Damping coefficient  $\Delta$  [ $\text{m}^{-1}$ ] vs. frequency [Hz]. Comparison between saturated (----- stearic acid methyl ester SME), mono-unsaturated (..... oleic acid methyl ester OLME), and tri-unsaturated (————— linolenic acid methyl ester L3ME) carboxylic acid methyl esters.

effect may impede repairing of wave-induced holes within the surface film, similar to the effect already described for TDME. Another consequence of the reduced cohesion between unsaturated alkyl chains are different characteristic Langmuir-curves: whereas OLME shows a curve typical for a liquid expanded phase state, SME approaches a condensed phase state curve. The more pronounced wave damping ability of the latter substance would be consistent with the previously mentioned observation that the change of a liquid expanded phase state (PBUE) to a condensed state (PCEE) leads to an increase in wave damping.

Even though elaidic acid derivatives have not yet been found in natural surface films it is interesting from a theoretical point of view to compare the wave damping effect of C=C-Z configurated acids (OLME) with C=C-E-configurated ones (elaidic acid methyl ester [ELME]). As shown in Figure 9, no difference between both forms is discernible. At first glance, this result was surprising because the C=C-E-form (ELME) was thought to be more compressible on account of a closer packing of the alkyl chains similar to that of a saturated compound (SME), which in turn was expected to lead to different wave damping characteristics compared to OLME. The Langmuir-curves of ELME and OLME, however, are very similar (Fig. 10) and consistent with nearly the same wave damping effect.

The presented data of methyl esters of the homologous series of carboxylic acids encouraged us to investigate a mixture of carboxylic acid methyl esters containing



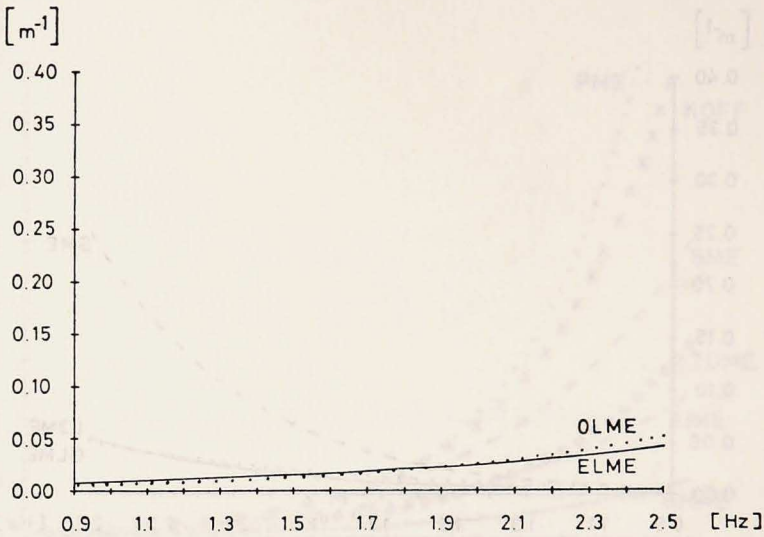


Figure 9. Damping coefficient  $\Delta$  [ $\text{m}^{-1}$ ] vs. frequency [Hz]. Comparison between C=C Z-form (..... oleic acid methyl ester OLME) and C=C E-form (————— elaïdic acid methyl ester ELME).

the same composition of fatty acids as has been found in natural surface films during the KOFF experiment (*Kombiniertes Oberflächenfilm Experiment* = joint surface film experiment) (station 2) (Kattner and Brockmann, 1978). The relative quantities of fatty acids in percent are given in Table 2. The actual carboxylic acid derivatives of the natural surface films are still unknown. It has been tentatively

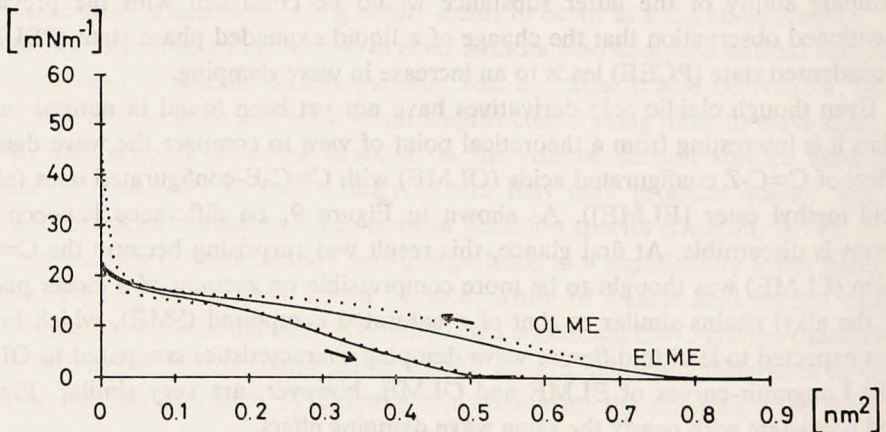


Figure 10. Langmuir-curves (surface pressure [ $\text{mNm}^{-1}$ ] vs. available area/molecule [ $\text{nm}^2$ ]) of oleic acid methyl ester (..... OLME) and elaïdic acid methyl ester (————— ELME).

Table 2. Relative quantities of fatty acids in percent as has been found during the KOFF experiment (station 2) (Kattner and Brockmann, 1978). The remaining 4.7% consist of traces of 16 carboxylic acids which have been neglected during this wave damping investigation.

fatty acid	rel. quantity (%)
12 : 0	4.2
14 : 0	14.4
16 : 0	32.3
18 : 0	37.9
20 : 0	0.5
14 : 1	0.9
16 : 1	1.4
18 : 1	3.6
18 : 3	0.1
	95.3

assumed all fatty acids exist as methyl esters which must not necessarily be in accordance with the *in situ* situation but allows preliminary investigation on the question to what extent the KOFF mixture of fatty acid alkyl chain length and unsaturated portion contributes to wave damping.

The result is also given in Figure 7. The KOFF mixture shows wave damping characteristics very similar to those of palmitic acid methyl ester [PME]. The absolute values lie between those of the main components, i.e., palmitic acid methyl ester [PME] and stearic acid methyl ester [SME]. The influence of derivatives with shorter and longer alkyl chains and with unsaturated C=C groups, which would lead to a significant lower damping effect as has been shown in the previous sections, can be neglected. In spite of the uncertainty concerning the alcohol component of natural carboxylic acid esters it can be concluded from these results that a strong direct wave damping effect is to be expected in the presence of natural surface films.

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